

**CORROSION SENSING MICROSENSORS**

This invention relates to microsensors for detecting corrosive media acting on a metallic material when mounted in situ adjacent a location in the metallic material.

Corrosion is a problem which leads to high maintenance and repair overheads in many different industries. The paper "Naval Aviation Corrosion Challenges and Solutions", Dale L. Moore, Corrosion 2000, paper 00270 (NACE, Orlando, USA, 2000) describes the problem areas in aircraft component corrosion and classifies corrosion types found in the aircraft industry.

Various different methods of detecting corrosion in a metallic material are known. The paper "Corrosion Detection and Monitoring – a Review", Vinod S. Agarwala, Siri Ahmad, Corrosion 2000, paper 00271 (NACE, Orlando, USA, 2000) describes various of the known methods, including visual methods, ultrasonic and acoustic methods, radiographic methods, thermal imaging, electromagnetic methods, electrical resistance measurement, and electrochemical methods. It describes a commonly used type of corrosion sensing, referred to as the electrical resistance probe method. In this case a sample of the material being monitored has its electrical resistance monitored. As the metal corrodes its cross section reduces and the resistance increases. In a practical embodiment of this technique the metal sample is made long and thin in order to optimise the resistance change to the thickness loss by corrosion. In this sensitive configuration the sensor is also highly sensitive to temperature changes by virtue of the material's temperature coefficient of resistivity. This is often overcome by using a second sample of the material of identical dimensions and temperature but protected from corrosion. Even when all these features are accommodated this sensor type is poor when the corrosion is at all localised, e.g. exfoliation, intergranular, pitting, crevice or stress corrosion. Under these conditions of degradation the resistance change is not proportional to extent of corrosion. Indeed it may not change sufficiently

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to allow problematic corrosion to be reliably detected. Localised types of corrosion cause significant problems for some types of metallic materials such as aluminium alloys.

The paper "Multi-layer Galvanic Cell for Next Generation Corrosion  
5 Sensors", M.D. Jaeger, B.R. Pilvelait, P.J. Magari, Corrosion 2000, paper 00302  
(NACE, Orlando, USA, 2000) describes a galvanic sensor with a multilayer  
geometry which is to be mounted in situ adjacent a location in a metallic  
material to be monitored and provides advantages in sensitivity and lifetime.  
The sensor measures the presence of an electrolyte, e.g. moisture in the area  
10 of the sensor, but not actual corrosion of the metallic material.

US patent 5338432 describes galvanic microsensors which use  
patterned thin metallic foils bonded to a non-conductive substrate. The sensors  
described include various alternative arrangements of interdigitated tracks of  
different metallic materials.

15 US patent 6383451 describes a thin film electric resistance sensor which  
includes a plurality of corrosive tracks exposed to corrosive media, running  
between two corrosion-protected common terminals. The detector described is  
sensitive to slight corrosion caused by pitting corrosion, however the current  
drain remains relatively high. In particular for corrosion monitoring in situ, it  
20 would be desirable to reduce the current drain in order to provide a longer  
battery lifespan; this is particularly important when a microsensor is to be  
mounted in a relatively inaccessible location and access thereto, for example for  
battery replacement, is to be avoided to as great an extent as possible. It would  
also be desirable to further improve the sensitivity and accuracy of the  
25 microsensor in detecting location-specific corrosion.

In accordance with one aspect of the present invention there is  
provided a microsensor for detecting corrosive media acting on a metallic  
material when mounted in situ adjacent a location in the metallic material, the  
microsensor including a plurality of corrosive tracks exposed to the corrosive  
30 media, each said corrosive track being formed as a patterned conductive thin

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film track and following a path which includes a plurality of bends, at least two of which are of opposite curvature.

The present invention in this aspect provides a highly miniaturised microsensor which can detect corrosion with high accuracy and reliability, whilst  
5 a relatively long lifetime of the microsensor and an associated limited power source are achievable.

Preferably, the thin film corrosive tracks are made of a material in which the proportion of the alloying constituent in the track material is similar to the proportion of the alloying constituent of the bulk metallic alloy to be monitored.  
10 This provides a microsensor which is capable of more accurately detecting corrosive phenomena acting on the bulk alloy than prior art thin film sensors, which include corrosive tracks made from a single metallic constituent, such as pure aluminium. Such single metallic constituent thin film tracks are not affected by corrosive media in the same manner as the bulk alloy, in particular  
15 when the bulk alloy is susceptible to localised corrosive phenomena.

Further aspects, features and advantages of the invention will become apparent from the following description of preferred embodiments of the invention given, by way of example, with reference to the accompanying drawings, wherein:

20 Figure 1 shows a resistive corrosion sensor in accordance with a first embodiment of the invention, in plan view;

Figure 2 shows a more detailed plan view of the formation of corrosive tracks in the corrosion sensor shown in Figure 1;

Figure 3 shows a galvanic corrosion sensor in accordance with a second  
25 embodiment of the invention, in plan view; and

Figure 4 shows a resistive corrosion sensor in accordance with a third embodiment of the invention, in plan view.

Various different embodiments of microsensor in accordance with the invention will now be described. The microsensors include corrosive tracks  
30 which mimic the corrosive characteristics of a bulk metal material, such that

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when placed in situ adjacent a location in a bulk metal material component, the effects of exposure to corrosive media measured by the microsensor reflect the effects of exposure of the bulk metal to the same corrosive media. The microsensors may be mounted in various locations and manners, for example by mounting between the plates of a joint between components, by adhesion to a component using a Mylar™ foil, etc. Once mounted, the microsensors may be coated with paint or another type of coating which similarly covers the bulk metal material.

Figure 1 shows a microsensor element including a resistive corrosion sensor 4 according to a first embodiment of the invention. The element includes a planar substrate 2 having an insulating surface provided for example by a layer of silicon oxide formed on a silicon base. The substrate 2 supports a thin film linear polarisation resistance (LPR) sensor 4, formed as thin film metallic patterns, and a thermocouple sensor 6 also formed as thin film metallic patterns. The LPR sensor 4 includes two common terminals 8, 10 formed side-by-side in parallel strips on the substrate 2, ending in respective connector stubs 12, 14, across which an output signal is sensed. The common terminals 8, 10 may be made of a metal which is highly resistant to corrosion, such as gold or platinum, and/or may be covered in a protective thin film to prevent exposure of the common terminals 8, 10 to corrosive media.

Between the common terminals 8, 10, a plurality of conductive thin film corrosive tracks 16 are formed. The corrosive tracks 16 are not covered by a protective thin film, and are thus exposed to corrosive media, when the microsensor is in use, to a similar degree to which the bulk metallic alloy material, adjacent to which the microsensor is mounted, is exposed in the mounting location.

Figure 2 shows a more detailed plan view of the formation of the corrosive tracks 16. Each corrosive track has a width  $W$  which is substantially constant, preferably to within 10% of the width, across its length. As an exemplary value, the width  $W$  of each corrosive track may be selected to be in the region of  $100\mu\text{m}$  in width.

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Each corrosive track 16 is formed to meander across a separate surface portion, in this embodiment one of a set of linear corridors 20, between the common terminals 8, 10. The track 16 extends fully across the corridor 20 in which it meanders. The corridors 20 each have a similar width  $D1$  and are  
5 separated by a distance  $D2$  such that the minimum separation  $D3$  between adjacent corrosive tracks is preferably at least as great as the track width  $W$ . Each corrosive track 16 has a periodically repeating serpentine shape within the linear corridor. As can be seen in Figure 2, the corrosive tracks 16 are formed from alternately inverted generally U-shaped bends  $B1, B2 \dots Bn \dots$  connected  
10 by track sections  $S1, S2 \dots Sn \dots$  spanning the centreline 22 of a corridor 20. The bends are alternately of opposite curvature. Each bend has a minimum radius of curvature  $R$  which is preferably greater than half the track width  $W$ . The spanning sections  $S1, S2 \dots Sn \dots$  are spaced from each other such that the sides of adjacent spanning sections are spaced by a distance  $C$  at the  
15 centreline, which distance is preferably greater than the track width  $W$ .

As a result of the serpentine shape of the corrosive track 16, the track gradually changes in direction, so that, using the centre line 22 as a reference axis, a track section of a positive or negative gradient relative to the centre line 22 is followed by a track section of an opposite gradient relative to the centre  
20 line 22, the two sections being to each side of a bend of the corrosive track. The gradients alternately vary as the track is followed through each bend. The serpentine paths thus resemble a periodic waveform.

By providing a serpentine path such as that described, the track length is increased without the need to increase the microsensor dimensions  
25 correspondingly, thus aiding miniaturisation. The sensitivity of the sensor is thus increased due to the increased track length and the current drain reduced. By using gradual bends having a minimum radius of curvature which is greater than half the track width as described, discrete or excessively sudden changes in direction of the path of the corrosive tracks, for example by the formation of  
30 right angles in the track paths, are avoided. It has been found that accelerated corrosion phenomena occur at such points in the track paths, which undesirably

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produce resistance variations which do not accurately reflect the state of corrosion of the component being monitored.

By maintaining at least a predetermined distance  $D_3$  between adjacent tracks, a predetermined minimum radius of curvature  $R$  at the bends, and at least a predetermined distance  $C$  between the adjacent track sections at the centre line, all track sections, including track sections within a single track and track sections within adjacent tracks, are well-spaced across the sensor. Preferably, no two adjacent track sections have sides spaced from each other by less than the track width  $W$ . In this way, corrosion effects are produced which more closely mimic the corrosion effects in the bulk alloy.

When mounted in situ, the effects of corrosion are monitored by intermittently passing a constant current across the common terminals and sensing the voltage response. After a period of exposure to corrosive media, whilst initially the tracking is fully intact and fully conductive, corroded track becomes gradually more resistive due to loss of conductive cross-sectional area and finally becomes insulating after corrosion affects at least one part of the track fully across its entire width. Different of the tracks may be affected differently by unrepresentative corrosive phenomena or other phenomena such as percussive damage, but by using a number of tracks, preferably at least four or more, connected in parallel, the response of the sensor more reliably reflects the effects of corrosion in the adjacent bulk metal.

The resistance thermometer 6 is made of a conductive material which is corrosively inert, such as platinum. The resistance thermometer 6 includes a tightly-concertinaed sensing section 17 which provides well-behaved measurable variations in resistivity with temperature, formed between connector stubs 18, 20. Since rates of corrosion are highly temperature-dependent, the output from the resistance thermometer can be used in combination with the output from the corrosion sensor to provide more accurate corrosion state prediction for the bulk alloy material being monitored.

The microsensor may also include other types of sensor, not shown, for measuring parameters which can have an effect on corrosion rates, such as an

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airflow sensor arranged for measuring airflow in the area in which the unit is mounted. Such an airflow sensor may be formed as thin film patterns of conductive strips, made of a material having a high temperature coefficient of resistivity, which are spaced in a direction in which airflow is to be sensed; variations in resistance of the strips indicate levels of airflow.

Figure 3 shows a microsensor element including a galvanic corrosion sensor 130 in accordance with a second embodiment of the invention. For the avoidance of unnecessary repetition, elements which are similar in arrangement and function to corresponding elements shown in Figure 1 are referenced with the same numerals in Figure 3, except incremented by 100, and the previous description of such elements should be taken to apply here.

In this embodiment, the corrosion sensor 130 is in the form of a galvanic corrosion sensor having interdigitated thin film tracks 132, 134 formed of different metallic materials and producing a measurable variation in galvanic voltage in response to exposure to an electrolyte. The thin film tracks 132, 134 are not covered by a protective thin film and are thus exposed to an electrolyte, which is a corrosive medium such as moisture, when the microsensor is in use, to a similar degree to which the bulk metallic alloy material, adjacent to which the microsensor is mounted, is exposed in the mounting location.

The thin film tracks include a first set of thin film tracks 132 and a second set of thin film tracks 134. The first set are made from a first metallic material connected to a first common terminal 108 and not connected to the second common terminal 110. The second set of thin film tracks 134 are made from a second, different, metallic material connected to the second common terminal 110 and not connected to the first common terminal 108. Preferably, the first set of tracks 132 are formed from a corrosive material mimicking the bulk metal for which the microsensor is to be used to monitor corrosion, and the second set of tracks 134 are formed from a relatively corrosively inert metal such as gold or platinum. Thus, a galvanic voltage is generated between the common terminals by the sets of corrosive tracks 132 and the set of non-corrosive tracks 134, which is measurable to provide an indication of time of exposure and amount of exposure to the electrolyte in the bulk material.

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The tracks 132, 134 are formed in the patterns described above in relation to Figure 2 in order to improve the performance of the sensor as described above.

Figure 4 shows a microsensor element including a resistive corrosion sensor 204B in accordance with a second embodiment of the invention. For the avoidance of unnecessary repetition, elements which are similar in arrangement and function to corresponding elements shown in Figure 1 are referenced with the same numerals and further referenced A or B respectively in Figure 4, except incremented by 200, and the previous description of such elements should be taken to apply here.

In this embodiment, the resistive corrosion sensor 204B is in the form of a referenced resistive corrosion sensor having a similar form to the resistive corrosion sensor described in relation to Figure 1. A further reference sensor 204A takes substantially the same form and is made of substantially the same material or materials as the corrosion sensor 204B, but is covered by a protective thin film layer and is thus not exposed to corrosive media when the microsensor is in use. In manufacture, the reference sensor 204A is first laid down and formed, followed by the protective layer, followed by the corrosion sensor 204B.

The corrosion sensor 204B is formed in an overlapping arrangement on top of the reference sensor. The function of the reference sensor 204A is to provide an output which is independent of corrosion but which has a virtually identical temperature-dependence in resistivity as the corrosion sensor 204B, due to its similar patterning and composition. The output from the reference sensor 204A can thus be used to balance out any temperature dependence in the output of the corrosion sensor 204B in a simple manner. By arranging the two sensors in an overlapping manner, rather than side-by-side, the temperature of the corrosion sensor 204B and the reference sensor 204A are more closely matched, in particular when mounted in locations subject to relatively large temperature gradients. Hence, the function of the reference sensor 204A is improved. Furthermore, miniaturisation of the microsensor element is improved.



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The two sensors 204A, 204B are arranged with a slight offset, and the corrosive tracks 216B and the corresponding tracks 216A are formed with a greater pitch. Thereby, the corrosive tracks 216B of the corrosion sensor are not formed on the surface of the protective film covering the corresponding tracks 216A of the reference sensor; this avoids degradation of the uniformity of the corrosive tracks 216B due to variations in surface height of the protective layer due to the tracks 216A underneath. In this embodiment, the number of tracks in each sensor is half that of the sensor shown in Figure 1, which provides a microsensor element of similar size, however larger numbers of elements may be provided by increasing the length of the common terminals 208A, 210A; 208B, 210B.

Note that, in relation to Figures 1, 3 and 4, thin film wiring patterning, or other types of wiring, connecting the sensor connector stubs in a microsensor unit, although not shown, is to be understood to be added. Further, protective coatings are not shown in the Figures, although, as described above, may be used to selectively protect parts of the surface of the microsensor element.

In particular envisaged applications, the bulk metal material to be mimicked is a metallic alloy and in such cases the material used for the corrosive tracks in each of the above-described embodiments is preferably an alloy having alloying constituents in similar proportions to the respective bulk alloy being mimicked. It has been found that the proportion of each alloying constituent of the track material is generally preferred to be accurate within 3%, more preferably within 1%, of the total constituents of the bulk alloy. Constituents having a proportion of less than 1% of the bulk alloy may either be present in a similar proportion, or omitted.

In preferred embodiments, in which the microsensor is to be used in a health monitoring system for aircraft, the corrosive tracks are made of an aluminium alloy, such as an aluminium copper alloy, an aluminium silicon alloy, an aluminium silicon copper alloy, etc. In particular, the material used for the corrosive tracks is preferably an alloy which closely resembles in composition one of the aluminium alloys used in the aviation components.

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In a first example the track alloy is an aluminium-copper alloy having a copper constituent proportion forming in the region of 2% to 8%, preferably approximately 5%, of the mass of the alloy, such as a 2000 series aluminium alloy.

5        In a second example the track alloy is an aluminium-silicon alloy having a silicon constituent proportion forming in the region of 5% to 20%, preferably approximately 12%, of the mass of the alloy, such as a 4000 series aluminium alloy.

10       In a third example the track alloy is an aluminium-magnesium alloy having a magnesium constituent proportion forming in the region of 2% to 8%, preferably approximately 5%, of the mass of the alloy, such as a 5000 series aluminium alloy.

15       In a fourth example the track alloy is an aluminium-magnesium-silicon alloy having magnesium and silicon proportions each forming in the region of 0.3% to 1.2% of the mass of the alloy, such as a 6000 series aluminium alloy.

In a fifth example the track alloy is an aluminium-zinc alloy having a zinc constituent proportion forming in the region of 2% to 8%, preferably approximately 5%, of the mass of the alloy, such as a 7000 series aluminium alloy.

20       In a sixth example the track alloy is an aluminium-lithium alloy having a lithium constituent proportion forming in the region of 1% to 4%, preferably approximately 2%, of the mass of the alloy, such as an 8000 series aluminium alloy.

25       Note that alloying constituents other than those specifically mentioned in each example above, and in lesser proportions to those specifically mentioned, may also be present in the alloys from which the tracks are made, particularly if present in the bulk alloys to be mimicked. These other alloying constituents may include one or more of magnesium, copper, manganese, silicon, iron, zinc, lithium, titanium, chromium, vanadium, zirconium, etc.

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The thin film layers from which the corrosive tracks are made is preferably deposited on the substrate by sputtering. In order to further improve the degree to which the corrosive characteristics of the thin film tracks mimic the bulk alloy, the thin film layer is preferably annealed following sputtering to encourage growth of metallic grains within the thin layer to produce a thin film which is essentially a two-dimensional array of metallic grains. Enhancing the grain size after sputtering by annealing enhances the capability of the sensors to specifically detect localised corrosion, at the early stages of its growth. Since localised corrosion initiates at specific sites such as grain boundaries, specific intermetallic phases etc, production of thin films of metal alloys with similar compositions of the intermetallic phases and grain boundaries of the bulk metal alloys concerned enhances detection of such localised corrosion. By subsequent photolithographic patterning, the films are structured into track forms, as described above, that give a desired sensitivity to such corrosion.

The thickness of the corrosive tracks is selected in accordance with the material from which the tracks are formed and the type of application for the microsensor. For example, for monitoring components in a marine environment the rate of corrosion is relatively high, and therefore a relatively thick film is used, for example, in the case of an aluminium alloy, corrosive tracks in the region of 50 $\mu$ m to 500 $\mu$ m in thickness are used. However, for other applications in which the environment in which the microsensor is to be placed is less corrosive, higher sensitivity to corrosion is required, and therefore thinner films are used to form the corrosive tracks. In the case of monitoring non-marine aircraft components, the thickness of the corrosive tracks is preferably between 0.5  $\mu$ m and 10  $\mu$ m, for example approximately 1.5 $\mu$ m.

The above-described geometries of the corrosive tracks may be used at any point in a range of miniaturisation scales. A track width of approximately 1 $\mu$ m is possible, and highly sensitive in the range of scales envisaged. However, such a track width will produce a sensor which is generally too sensitive for practical corrosion sensing applications. Track widths of up to 1mm are envisaged. Preferred track widths fall within the range 20 $\mu$ m to 500 $\mu$ m.

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In a further embodiment, not shown in the Figures, at least two of the different sensor configurations shown in Figures 1, 3 and 4 are formed on a single substrate, so as to provide a microsensor unit having a plurality of sensor outputs giving different indications of corrosion in a single location.

5 In a further embodiment, not shown in the Figures, sensors having tracking arranged as described and of different widths in each sensor, for example different by an order of magnitude, are formed on a single substrate and included in a single microsensor unit, so as to provide so as to provide a microsensor unit having a plurality of sensor outputs of different sensitivities to  
10 corrosion and different sensor lifetimes. A sensor having a smaller track width will be more sensitive but have a smaller lifetime; once the sensor has degraded a sensor having a larger track width may be used to continue corrosion monitoring at a lower sensitivity.

In a yet further embodiment, not shown in the Figures, sensors having  
15 tracking arranged as described and of a plurality of different metallic compositions of different corrosivities are formed on a single substrate and included in a single microsensor unit, so as to provide different sensitivities to corrosion and different sensor lifetimes. For example, a first sensor having tracking made of a material which is relatively corrosive, such as an aluminium-silicon-copper alloy, may be included for higher sensitivity to corrosion but have  
20 a smaller lifetime, and a second sensor having tracking made of a less corrosive material such as substantially pure aluminium may be included for longer lifetime corrosion detection at a lower sensitivity. A third sensor having tracking made of a material having an intermediate corrosivity such as an  
25 aluminium-silicon alloy may also be included for medium lifetime corrosion detection at a medium sensitivity

The corrosion microsensors described herein are located on various different components of a multi-component apparatus, such as an aircraft, to form a corrosion sensing system, which itself is part of a health monitoring  
30 system for the apparatus. Typically, the components of the apparatus will be formed from different metal alloys, in particular, in the case of an aircraft, from different aluminium alloys such as the examples given above. One aspect of

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the invention is that a plurality of different corrosion microsensors, each having a set of corrosive tracks made of different metal alloy compositions mimicking the different component material compositions, are mounted adjacent locations in the respective corresponding components to form part of the corrosion sensing system for the apparatus.

A corrosion sensing system arranged in accordance with the present invention includes a data processing system arranged to receive data derived from each of a plurality of microsensor units which contain the corrosion sensors, to process the detection data and to provide corrosion analysis data based thereon, whereby corrosion state prediction is provided for the bulk alloy materials of the various different components in the various different locations being monitored. The units include a battery and a sensing circuit for each sensor. In the case of the LPR sensor, the circuit is adapted to apply a constant current to common terminals of the sensor, and to measure a voltage generated therein to sense resistance changes in the sensor. In the case of the galvanic sensor, the circuit is adapted to sense the galvanic voltage generated across the two common terminals.

One or more of the corrosion sensors of the present invention may be included in a semi-autonomous microsensor unit which includes a data logging memory, for storing sensor data sensed at a plurality of intervals over a period of time, and a data output whereby data is output from the microsensor unit to the data processing system. Such a semi-autonomous microsensor unit may be connected to the data processing system by means of physical wiring through which data is communicated, or may include a data port whereby a data connection is intermittently established. The data port may be a socket to which a data cable of a reader unit is manually connected, or a wireless data port such as a Bluetooth™ short range radio transmitter.

The above embodiments are to be understood as illustrative examples of the invention. Further embodiments of the invention are envisaged. Note for example that, whilst the corridors across which the corrosive tracks extend are in the above-described embodiments linear, the

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corridors may instead take a different form, including various different curved forms, including bell-shaped forms.

Using thin film alloys to mimic the behaviour of bulk alloys lends itself to further applications in corrosion both to elucidate corrosion rates specific to  
5 specific components and locations thereon, in which the microsensor is mounted. It should be noted that the invention is applicable to alloy systems other than aluminium, including magnesium alloys, which are used in the manufacture of gearbox components. It has particular benefit for alloys which tend to corrode locally, such as by exfoliation, or intergranular, pitting, crevice or  
10 stress corrosion.

It should be understood that the above-described preferred geometries, in particular the track width values, the track section separation values and the minimum radii of curvature values, have been found by empirical observation. Experiments were conducted in which the corrosion rates of large numbers of  
15 different test geometries were compared with the corrosion rates of the bulk metal materials being mimicked, when exposed to the same corrosive media. Geometries inside or outside the thresholds described were found to tend to cause corrosion effects which did not accurately reflect those in the bulk material; however it should be understood that, if different sensor characteristics  
20 are desired, for example increased sensitivity to corrosion relative to the bulk material, such alternative geometries may be used.

It is to be understood that any feature described in relation to any one embodiment may be used alone, or in combination with other features described, and may also be used in combination with one or more features of  
25 any other of the embodiments, or any combination of any other of the embodiments. Furthermore, equivalents and modifications not described above may also be employed without departing from the scope of the invention, which is defined in the accompanying claims.